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COMMENTARY

Conformations of Linear Chains. Systematics and Suggestions for Nomenclature

ABSTRACT

There are six categories of calculated favored dihedral angles in linear M_nX_{2n+2} chains. The Prelog−Klyne nomenclature is not helpful for classifying them, and we propose the following labels and symbols: A, anti, reserved for torsional angles within a few degrees of 180°; T, transoid, $\omega \simeq 165°$; D, deviant, $\omega \simeq 150°$; O, ortho, $\omega \simeq 90°$; G, gauche, $\omega \simeq 60°$; C, cisoid, $\omega \simeq 40°$. With the exception of C, all of these categories have been observed in alkanes, perfluoroalkanes, or oligosilanes.

In introductory organic chemistry texts, conformational minima are described for *n*-butane. The preferred torsional angles ω are 180° (anti, A) and ∼±60° (gauche, G).[1] These minima are due to the existence of intrinsic rotational barriers around single bonds, present even in ethane.[2] This simple and generally recognized situation applies when the lateral substituents on a linear chain are very small, e.g., in *n*-alkanes and oligosilanes, as observed[3] in polyethylene and calculated[4] for polysilane, $(SiH_2)_n$, but it has recently become clear that it is not general for M_nX_{2n+2} chains.[5,6]

In very severely crowded chains (e.g., X = *tert*-butyl[7]), in those in which some backbone valence angles are smaller than tetrahedral (e.g., thioethers[8]), and in other more complex cases, deviations from the usual 180° and ±60° angles are frequent, and the Prelog−Klyne nomenclature[9,10] is then standard: 0° < |ω| < 30°, syn-periplanar (sp); 30° < |ω| < 90°, synclinal (sc); 90° < |ω| < 150°, anticlinal (ac); 150° < |ω| < 180°, antiperiplanar (ap). Potential energy minima at the borderline values, |ω| = ∼90° and ∼150°, are unfortunately common in M_nX_{2n+2} chains with substituents X larger than H, making this notation unhelpful. This has contributed to a proliferation of symbols and notation for the conformations of polysilanes, Si_nX_{2n+2}. The purpose of this comment is to point out the existence of six quite clear-cut categories of favored dihedral angles in M_nX_{2n+2} chains with X ≠ H, such as perfluoroalkanes and polysilanes, and to suggest a set of labels that preserves as much as possible of the current usage (we recognize that our list may not exhaust future intermediate conformations).

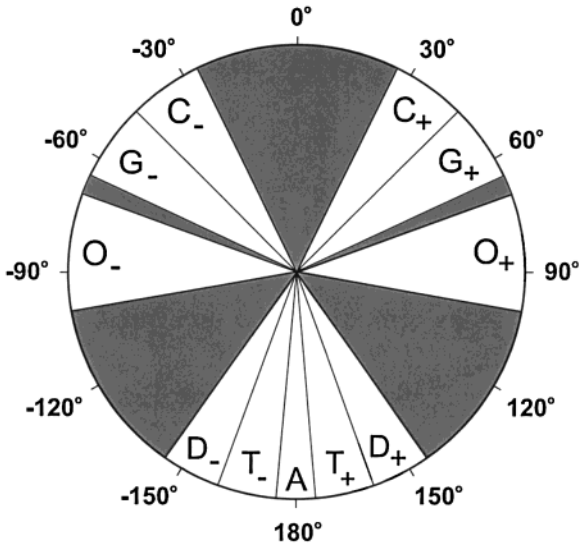

FIGURE 1. Favored dihedral angles and their proposed labels.

As the size of the substituents X in an oligomeric or polymeric linear chain $(MX_2)_n$ is increased relative to the M−M bond length, repulsive interactions between X atoms in backbone positions 1 and 3 become important. It has long been recognized[11] that the exactly planar A geometry then becomes a transition state between two minima with $\omega \simeq \pm 165°$. In $(MX_2)_n$ chains, these structures have been calculated for permethylated oligosilanes[12] and observed for perfluorinated polyethylene,[13] which has two crystalline forms with $\omega \simeq 166°$ and 168°. We will term these conformations *transoid*, T.

Similar interactions between groups X located in backbone positions 1 and 4 lead to a splitting of the gauche states into minima with $\omega \simeq \pm 55°$ (G) and ∼±90°(*ortho*, O).[14,15] Until recently there has been little experimental evidence for the

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O conformation in M_nX_{2n+2} chains,[16] but it has now been observed directly in C_4F_{10}[17] and Si_4Cl_{10},[18] and is also calculated to exist in C_4Me_{10}, Si_4Me_{10}, and $Si_4(SiH_3)_{10}$.[5]

For longer alkyl substituents X, the situation becomes even more complicated.[19] Now, not only the CH_2 group next to the backbone, but also the neighboring one may be involved in interactions between substituents. As a result, for particular local conformations of the alkyl substituents, in molecules such as $Me_3Si-SiEt_2-SiEt_2-SiMe_3$ certain T and G minima are calculated to disappear, and in their place appear new conformations with greatly reduced dihedral angles. For these, we have proposed[6] the labels *deviant*[20] (D, $\omega \simeq 150°$) and *cisoid*[21] (C, $\omega \simeq 40°$). The crystalline polymers [(*n*-butyl)$_2$Si]$_n$ and [(*n*-pentyl)$_2$Si]$_n$ are known to adopt a helical conformation with $\omega \simeq \pm 154°$ (approximately a 7/3 helix),[22] which we identify as D, but no observations of the C conformation have been reported so far.

For many polymers, the distinction between A, T, and D, or O, G, and C conformations may seem unimportant, because easily observed polymer properties other than the crystal structure may not depend greatly on the backbone conformation. It is known from experiments[23] and calculations[24] that the $\sigma-\sigma^*$ excitation energy depends strongly on the backbone conformation, but many saturated polymers absorb only in the vacuum UV, and little is known about their electronic spectra. However, polysilanes, polygermanes, and polystannanes absorb in the near-UV region. Their readily observable first $\sigma-\sigma^*$ absorption peak shifts dramatically to the blue as the backbone dihedral angle ω is reduced from 180° to smaller values, and this is easily understood in simple terms.[25] The existence of A, T, and D bond conformations, and of conformations involving mixtures of these rotational states, probably explains the multiplicity of ordered phases with differing UV maxima, observed recently for several polysilanes.[26,27]

Listed in Figure 1 is the entire array of presently recognized, permitted rotational minima and the symbols which we suggest for use in describing these conformations: A, anti, reserved for torsional angles within a few degrees of 180°; T, transoid, $\omega \simeq 165°$; D, deviant, $\omega \simeq 150°$; O, ortho, $\omega \simeq 90°$; G, gauche, $\omega \simeq 60°$; C, cisoid, $\omega \simeq 40°$. With the exception of the planar A conformer, these backbone conformations are all chiral and appear as enantiomeric pairs. If the members of the pairs need to be referred to individually, we recommend notation such as T_+ (right-handed helix, $\omega \simeq +165°$) and T_- (left-handed helix, $\omega \simeq -165°$).

The dark segments in Figure 1 indicate that bond eclipsing does not occur in stable conformers of linear chains. In certain constrained systems it is observed, however, and we propose the labels S, syn, for $\omega \simeq 0°$ and E, eclipsed, for $\omega \simeq 120°$.

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